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GROUP IB ORGANOMETALLIC CHEMISTRY

XXXII *. ARYLCOPPER COMPOUNDS Ar_nCu_n AS INTERMEDIATES IN ORGANOMETALLIC SYNTHESIS. SINGLE-STEP SYNTHESIS AND DYNAMIC NMR SPECTROSCOPY OF DIORGANOTIN DIHALIDES $Ar_{2-n}R_nSnX_2$ (Ar = 2-$Me_2NCH_2C_6H_4$ OR (*S*)-2-$Me_2NCHMeC_6H_4$; n = 0 OR 1) **

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Summary

The selective, single-step synthesis of (2-$Me_2NCHZC_6H_4$)$RSnX_2$, in which Z = H or Me, R = Me or Ph and X = Cl or Br, starting from the tetranuclear copper cluster compound (2-$Me_2NCHZC_6H_4$)$_4Cu_4$ and $RSnX_3$ is described. Reaction of (2-$Me_2NCH_2C_6H_4$)$_4Cu_4$ with $SnBr_4$ in a 1/2 molar ratio afforded (2-$Me_2NCH_2C_6H_4$)$_2SnBr_2$ in almost quantitative yield.

^{1}H NMR spectroscopic data of these novel compounds, which are monomeric in solution, indicate that: (i) intramolecular Sn—N coordination renders the Sn atom in (2-$Me_2NCHZC_6H_4$)$RSnX_2$ pentacoordinate, with the organo ligands residing in the equatorial plane of a trigonal bipyramidal structure, and the Sn atom in (2-$Me_2NCH_2C_6H_4$)$_2SnBr_2$ hexacoordinate, with *trans* organo groups and a *cis* arrangement for the Br and the N atoms, (ii) in pyridine the Sn atom in (2-$Me_2NCHZC_6H_4$)$RSnX_2$ becomes hexacoordinate by complex formation with the solvent but that intramolecular Sn—N coordination has been retained.

The stereochemical lability of the pentacoordinate Sn center in the diorganotin dihalides (2-$Me_2NCHZC_6H_4$)$RSnX_2$, which contain a dissymmetrical equatorial plane, has been established on the basis of the dynamic NMR spectra of

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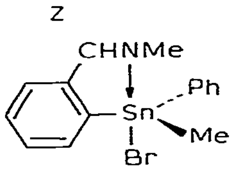
[*] For Part XXXI See ref. 1.

[**] Dedicated to Professor H. Normant on the occasion of his 72nd birthday on June 25th, 1979.

[(*S*)-2-$Me_2NCHMeC_6H_4$]$MeSnBr_2$, (which contains a C-chiral label with a stable configuration), as well as by the spectra of mixtures of (2-$Me_2NCH_2C_6H_4$)Me-SnX_2 (X = Cl and Br)

Introduction

In previous papers we have shown that aryl groups bound to copper enter readily into exchange reactions with Sn—X bonds of organotin halides $R_{4-n}SnX_n$ (n = 2, 3 or 4) [2—4] Single-step syntheses of novel types of chiral pentacoordinate triorganotin halides ArMePhSnX [3] or (*S*)-ArMePhSnX [4] (2-$Me_2NCHZC_6H_4$ Ar, Z = H, (*S*)-Ar, Z = Me) have been achieved by using arylcopper cluster derivatives Ar_4Cu_4 [5] and (*S*)-Ar_4Cu_4 [4]



I Z = H
II, Z = Me

X-ray analysis of II [4] and of the diphenyltin derivative $ArPh_2SnBr$ (III) [6] confirmed a distorted trigonal bipyramidal geometry for the central tin atom in these compounds, with the organic ligands residing in the equatorial plane while the electronegative Br and N atoms occupy axial positions

Compounds I and II have a chiral tin center ^1H NMR studies revealed that, in solution, inversion at tin is slow on the NMR timescale, but fast on the laboratory timescale However, by preferential crystallization, the optically pure $(S)_C(S)_{Sn}$-diastereomer of II could be isolated and studied [4]

In the dynamic NMR studies of I and II both the CH_2N protons and the NMe_2 groups are used as probes for the detection of chirality at the tin center as well as for the occurrence of intramolecular Sn—N coordination In this paper we describe the application of these results to a study of the nature of the diorganotin dihalides $ArRSnX_2$ in which Ar contains a prochiral (CH_2NMe_2) or C-chiral ($CHMeNMe_2$) *ortho*-substituent. Attention will be given to the selective single-step synthesis of pentacoordinate (2-$Me_2NCHZC_6H_4$)$RSnX_2$ and hexacoordinate (2-$Me_2NCH_2C_6H_4$)$_2SnBr_2$ compounds

Results

Synthesis of (2-$Me_2NCHZC_6H_4$)$RSnX_2$ and (2-$Me_2NCH_2C_6H_4$)$_2SnBr_2$

Addition of the tetranuclear arylcopper compounds IV and V to a solution of an organotin trihalide in a : 4 molar ratio gave rise to the formation of the corresponding organotin dihalides in nearly quantitative yields. Similarly, reaction of Ar_4Cu_4 (IV) with $SnBr_4$ in a 4 : 2 molar ratio resulted in the quantitative formation of Ar_2SnBr_2 (X).

The novel tin compounds VI—X are white solids which according to osmometric molecular weight determination exist in benzene (VI-IX) or in $HCCl_3$ (X) as discrete monomers.

The ^1H NMR data are given in Table 1.

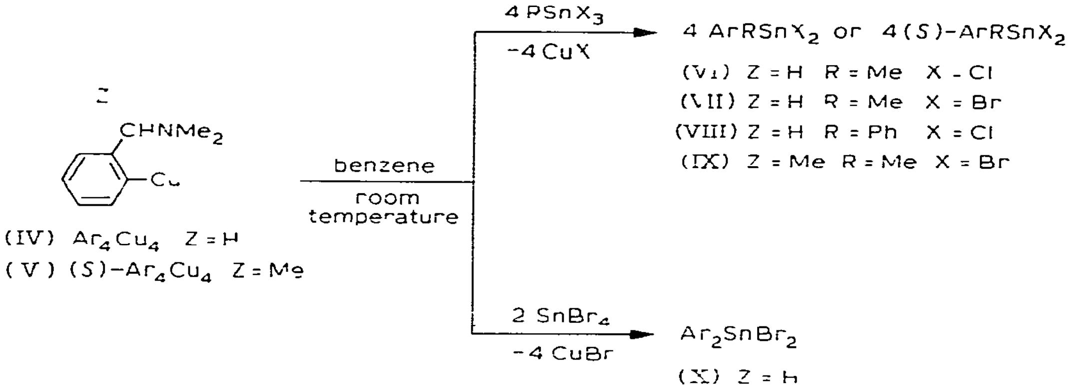


TABLE 1

^{1}H NMR SPECTRA OF DIORGANOTIN DIHALIDES VI—X AND OF THE PENTACOORDINATE TRIORGANOTIN HALIDES I AND II

Compound	Solvent (Temp °C)	δ [a]				
		NMe_2	NCH_2	Sn—Me	^2J(Sn—CH)	H_6 [b]
VI $ArMeSnCl_2$	Tol-d_8(Amb)	1 65s	3 03s	0 80s	76/80	8 37(96)
	Pyr-d_5(Amb) [c]	2 50s	3 90s	1 60s	102/107	7 95
	Pyr-d_5(—40) [c]	2 58s [d]	3 91 [d] 4 12 [d]	1 73		
		2 78s [d]		1 76		
VII $ArMeSnBr_2$	Tol-d_8(Amb)	1 65s	3 02s	1 00s	76/80	8 44(96)
	Pyr-d_5(Amb) [c]	2 55s	3 93s	1 65s	102/107	7 95
VIII $ArPhSnCl_2$	Tol-d_8(Amb)	1 79	3 02	—	—	8 65(96)
	Tol-d_8(—95)	0 95s [e]	2 44 [e] 2 90 [e]	—	—	
		1 64s [e]				
	Pyr-d_5(Amb) [c]	2 43	4 00	—	—	8 61
IX (S)-$ArMeSnBr_2$	Tol-d_8(Amb)	1 50s 1 85s	[f]	1 10s	75/79	8 55(96)
	Tol-d_8(105) [g]	1 80s	—	1 15s	75/79	
	Pyr-d_5(Amb)	2 30s 2 70s	[h]	1 95s	98/102	8 05
X Ar_2SnBr_2	$CDCl_3$(Amb)	2 15s	3 25d [i] 4 15d [i]	—	—	8 20(108)
	$CDCl_3$(—50) [j]	2 00s 2 60s	3 25d [i] 4 15d [i]	—	—	
	Pyr-d_5(Amb)	2 20s	3 30d [i] 4 15d [i]	—	—	8 42(104)
I ArMePhSnBr [k]	Benz-d_5(Amb)	1 45s	2 81d 3 02d	0 87	65/68	8 72
	Pyr-d_5(Amb)	1 87s	3 38d 3 39d	1 16	65/68	8 72
II (S)-ArMePhSnBr [k]	Benz-d_5(Amb)	1 36s	—	0 91	67/65	8 95
	Pyr-d_5(Amb)	2 04s	—	1 10	67/65	8 88
VI/VII (3/1)	Tol-d_8(Amb)	1 70s	3 10s	0 90	76/80	8 36
	Tol-d_8(—95)	1 70 [e]	3 10 [e]	0 80	76/80	
				1 00		

[a] TMS internal δ(ppm) ^2J(Sn—H) in Hz [b] Multiplet resonances values listed are the centers of the multiplets Value between parentheses is $^3J(Sn—H_6)$ in Hz [c] All resonances are broadened [d] Broadened resonances with peak heights of the low-field resonances of NMe and NCH_2 larger than the high-field peaks approximate ratio 3 1 [e] Broad resonances T_{coal} ~—90°C [f] δ(α-CH_3) 0 83(d J_{AB} 7 Hz) δ(α-H) 3 44 (q) [g] T_{coal} NMe singlets ~+58°C. [h] δ(α-CH_3) 1 35(d) δ(α-H) 4 63(q) [i] J_{AB} 14 Hz [j] T_{coal} NMe singlets ~0°C [k] See refs 3 4

Discussion

The syntheses of VI—X provide a further illustration of the surprising selectivity of polynuclear arylcopper compounds when used as intermediates in organometallic synthesis. The arylation of R_nSnX_{4-n} occurs stepwise with high selectivity, and allows the synthesis of R_3SnX [2—4] and R_2SnX_2 compounds in a single step. Which particular feature of the copper clusters used (e.g. formation of new, less reactive $R_{m-n}Cu_mX_n$ clusters [2,7] in the metal—halogen exchange, or the presence or absence of built-in ligands) accounts for this high selectivity is a subject which will require further explorative work.

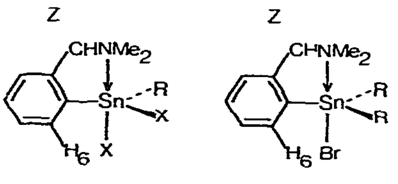
The structure of (2-$Me_2NCHZC_6H_4$)$RSnX_2$ in solution

Because diorganotin dihalides are generally stronger Lewis acids than triorganotin halides [8], the intramolecular Sn—N coordination which was observed earlier in the corresponding triorganotin halides I—III must also be expected to occur in compounds VI-IX. The observed molecular weights exclude the possibility of intermolecular Sn-halogen coordination [9]. On this basis, the Sn atom in the compounds (2-$Me_2NCHZC_6H_4$)$RSnX_2$ (VI—IX) is pentacoordinate. A trigonal bipyramidal structure in which the aryl and R groups reside in the equatorial plane is most likely, cf. refs. 2—4, 6. The bite of the 2-Me_2NCHZ-C_6H_4 ligand (C—Sn—N angle in II, 75.2° and in III, 75.3° [4]) dictates that the amino ligand will occupy an axial position [10] leaving one equatorial and one axial position for the two bromine atoms (cf. Fig. 1a).

Large downfield shifts of the signal for H_6 to about δ 8.5 ppm are observed in the spectra of VI—IX. Together with the earlier observation of similar shifts for the H_6 protons in the pentacoordinate triorganotin compounds I—III, this forms a strong argument for the similarity of the structures of these compounds, see Fig. 1. These large downfield shifts are a result of the axial—equatorial spanning of the bidentate 2-$Me_2NCHZC_6H_4$ group, which brings the H_6 proton close to the halogen atom in the axial site *trans* to the amino ligand. It is interesting to note that the nonbonding $H_6 \cdots X$ distance in II was calculated from the X-ray data to be 2.80 Å [4].

The methyl—Sn resonances in the spectra of the (2-$Me_2NCHZC_6H_4$)$MeSnX_2$ compounds (VI, VII and IX) are observed at about 1 ppm and show $^2J(Sn—CH_3)$ values of about 76 Hz, which is near the upper limit found for pentacoordinate methyltin species [9].

The NMR data for compounds VI—IX recorded as solutions in pyridine are



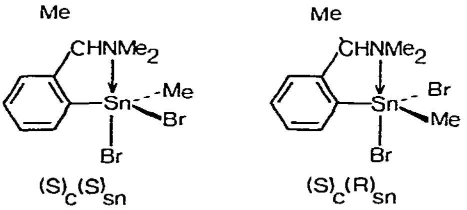
a b

Fig. 1. Trigonal bipyramidal structures of (a), diorganotin dihalides and (b) triorganotin halides [2—4] as a result of intramolecular Sn—N coordination

shown in Table 1 The respective CH_2N, NMe and SnMe resonances undergo a large solvent-induced downfield shift which is comparable to the solvent dependence observed for the corresponding triorganotin halides I—III [2—4] In the case of a solvent-solute interaction, the preferential orientation of the benzene or pyridine molecules at the site of the built-in ligand will be comparable, as can be deduced from the very similar shifts of ArMePhSnBr (I) and (*S*)-ArMePhSnBr (II), see Table 1 However, in the spectra of the diorganotin dihalides VI—IX the H_6 resonance shifts strongly upfield (about δ 0 5 ppm, see Table 1) upon changing the solvent from toluene to pyridine Whereas the $^2J(Sn—CH_3)$ values of 65/68 Hz for the triorganotin halides I and II do not change upon changing the solvent from benzene to pyridine, the $^2J(Sn—CH_3)$ values for the diorganotin dihalides VI, VII and IX increase from 76/80 Hz in toluene to 102/107 Hz in pyridine These results indicate that the pyridine molecule resides in the coordination sphere of the tin atom, resulting in a hexacoordinate geometry with *sp*-hybridization of the tin atom (cf ref 9) Assuming retention of the intramolecular Sn—N coordination bond in pyridine (cf retention of this bond in I and II when dissolved in pyridine [3,4]) the complexes formed can be of the type $(2\text{-}Me_2NCHZC_6H_4)RSnX_2Py$ or $[(2\text{-}Me_2NCHZC_6H_4)RSnXPy_2]X$ At low temperature (—40 to —95° C) the resonance pattern de-coalesces into two patterns which have an intensity ratio of ~3/1, see Table 1 This ratio is sensitive to the concentration of the diorganotin dihalide in solution, pointing to the presence of at least two isomeric forms for these pyridine complexes which undergo inter- and intra-molecular exchange

The occurrence of pentacoordination as a result if intramolecular Sn—N coordination has been unambiguously deduced from the observation that the spectra of the C-chiral compound (*S*)-$ArMeSnBr_2$ IX at room temperature shows two singlets for the NMe_2 protons The NMe_2 groups in the C-chiral $CHMeNMe_2$ group are diastereotopic, and will thus appear in the spectrum as two singlets, when the nitrogen center is a stable pyramidal assembly This will only be the case when inversion at the nitrogen center is blocked by Sn-N coordination Furthermore, in the pentacoordinate situation, the equatorial plane is dissymmetric and can have either the $(S)_{Sn}$ or $(R)_{Sn}$ configuration [4], see Fig 2 Accordingly, two patterns arising from the two possible diastereomers $(S)_C(S)_{Sn}$ and $(S)_C(R)_{Sn}$ are expected in the slow exchange From the observation of only one pattern in the spectrum of IX it must be concluded that rapid inversion of configuration at the tin center occurs

$PhCl_2Sn(CH_2)_3C(O)Me$, in which intramolecular Sn—O coordination was



$(S)_C(S)_{Sn}$ $(S)_C(R)_{Sn}$

Fig 2 Possible diastereomers for {2-[1-(*S*)-(dimethylamino)ethyl]}methyltin dibromide

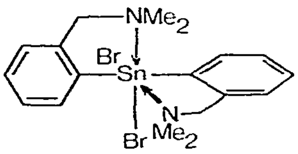


Fig. 3 Proposed structure for bis{2-[(dimethylamino)methyl]phenyl}tin dibromide

deduced from the shift of the ν(C=O) from 1670 to 1710 cm^{-1} in the corresponding 2,2'-bipyridine complex, is to our knowledge the only other reported example of a pentacoordinate diorganotin dihalide [12]

The structure of $(2\text{-}Me_2NCH_2C_6H_4)_2SnBr_2$ *in solution*

In view of the well-documented tendency of diorganotin dihalides to form 1 : 2 complexes with monodentate ligands [13], a hexacoordinate structure for Ar_2SnBr_2 seems likely, see Fig. 3 This is supported by the following observations. Only small shift differences for the respective resonances are observed when changing the solvent from $CHCl_3$ to pyridine This is compatible with a more symmetrical arrangement of the electronegative ligands in X as compared with VI—IX, resulting in a less specific solvent—solute interaction (see above) Furthermore, the observation of only one resonance pattern in the spectrum at —50° C, which consists of an AB pattern for the CH_2N protons and two singlets for the NMe protons, can only be explained by a *trans* arrangement of the organo ligands and a *cis* arrangement of two coordinated N-atoms and two Br-atoms. This structure lacks relevant symmetry planes passing through the prochiral benzylic C-centers (cf. the AB pattern) and through the stable pyramidal N-centers (cf two singlets) resulting in anisochronous resonances

The proposed specific ligand arrangement, i.e. *trans* R groups and *cis* Cl atoms, has earlier been proven by Mossbauer, NQR and dipole moment studies for adducts of the type $R_2SnCl_2L_2$ (L monodentate ligand) in the solid [8,11]

Dynamic behaviour of pentacoordinate $(2\text{-}Me_2NCHZC_6H_4)RSnX_2$ *and hexacoordinate* $(2\text{-}Me_2NCH_2C_6H_4)_2SnBr_2$

A comparison of the structures of the pentacoordinate $ArRSnX_2$ and hexacoordinate Ar_2SnX_2 in solution is of interest with a view to elucidating the nature of stereoisomerization processes in organotin halides containing built-in ligands.

Direct information concerning the occurrence of Sn—N coordination in the $ArRSnX_2$ compounds can be obtained from the compound (S)-$ArRSnX_2$ containing the C-chiral label $CHMeNMe_2$ (see above) At higher temperature, the two NMe singlets start to coalesce (see Fig 4), finally resulting in one sharp singlet above 60° C. The coalescense temperature T_{coal} of 58° C ($\Delta\nu$ 0 35 ppm) is considerably higher than the T_{coal} of 28° C ($\Delta\nu$ 0.41 ppm) observed for II [4]. This points to a stronger Sn—N bond in the diorganotin dihalides VI—IX as compared with the triorganotin halides I and II, this is as expected, in view of the stronger Lewis acidity of the diorganotin dihalides [13] The process by which the NMe singlets coalesce involves Sn—N bond dissociation with concomitant inversion at N and rotation around the C—N bond.

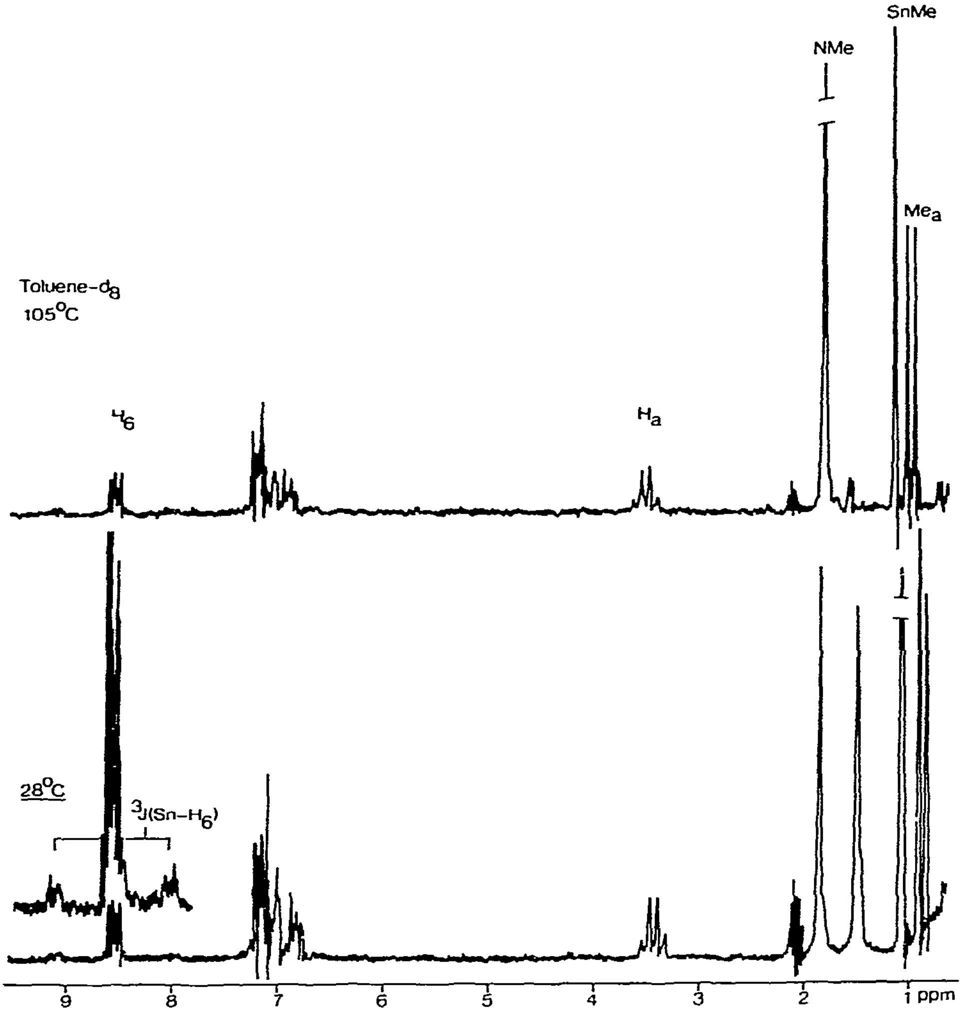


Fig 4 ${}^1H$ NMR spectrum (90 MHz) of {2-[1-(*S*)-(dimethylamino)ethyl]phenyl}methyltin dibromide in toluene-d_8

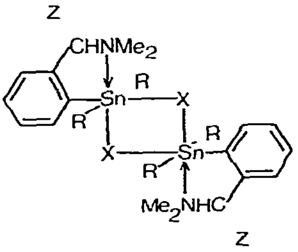


Fig 5 Proposed intermediate formed by association of two monomeric organotin halides R = Me or Ph R′ = organic group or halogen

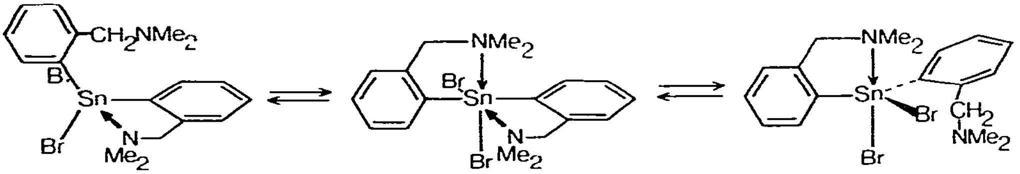


Fig. 6 Interconversion between pentacoordinate species resulting from Sn—N dissociation in hexacoordinate bis{2-[(dimethylamino)methyl]phenyl}tin dibromide

The fact that diastereomeric forms for (*S*)-ArMeSnBr$_2$ (see Fig 2) are not observed indicates that the configuration of the pentacoordinate tin center is labile on the NMR timescale. The observation that only singlets for the NMe$_2$ and CH$_2$N protons are observed in pentacoordinate (2-Me$_2$NCH$_2$C$_6$H$_4$)RSnX$_2$, which contains a dissymmetric equatorial plane, but lacks the C-chiral label, is likewise explained by the stereochemical lability of the Sn center in these compounds

Possible mechanisms which can account for the observed stereochemical lability are Berry-type pseudorotation processes [14] or processes involving Sn-X bond dissociation [4,15]. Such processes were excluded in our recent study of the stereoisomerization of II * [4] Instead, a mechanism involving stereoisomerizations, taking place in a dimeric intermediate with hexacoordinate tin centers, was proposed, see Fig. 5, X = R [4].

The results of NMR measurements on mixtures of ArMeSnCl$_2$ and ArMe-SnBr$_2$ in apolar solvents indicate that such a mechanism (see Fig 5, R′ = halogen) applies to the stereoisomerization of the pentacoordinate diorganotin dihalides.

$$\mathrm{ArMeSnCl_2 + ArMeSnBr_2 \rightleftharpoons [(ArMeSnX_2)_2] \rightleftharpoons 2\ ArMeSnClBr}$$

$$\mathrm{X{=}Cl\ and\ Br}$$

The NMR spectrum of a 1 1 mixture of ArMeSnCl$_2$ and ArMeSnBr$_2$ in toluene-d_8 shows only one resonance pattern, of which the Sn—Me resonance appears at a value between those of the starting compounds, cf. Table 1. Below —80°C, the broadened Me-Sn singlet de-coalesces into two singlets Moreover, the NMe$_2$ singlet and the CH$_2$N singlet start to de-coalesce, which indicates that, under these conditions, the tin center starts to become configurationally stable on the NMR timescale.

The dynamic behaviour of the Ar$_2$SnBr$_2$ compound is of interest in view of the stereoisomerization processes proposed to take place in Ar$_2$SnMeBr ** [3]. The ^{1}H NMR spectra at temperatures above —50° C show that the two NMe

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* Berry pseudorotation processes are energetically unfavorable because of the distinct site preference of the N and halogen atoms for axial positions [9] and the constraints of the five-membered chelate ring. Sn—X dissociation in the pentacoordinate compounds would result in opening of the C—Sn—N angle from 75° to a value of 109° which makes such a process unlikely

** ^{1}H NMR and Sn Mossbauer studies [16] revealed that Ar$_2$SnMeBr has a pentacoordinate structure both in solution and in the solid state, which is in line with the triorganotin halides being weaker Lewis acids singlets coalesce into one singlet, whereas the AB pattern for the benzylic protons is retained up to 50°C Stereoisomerization taking place in the hexacoordinate structure would result in simultaneous coalescence of both patterns This indicates that the diastereotopic NMe groups become homotopic as a result of Sn—N dissociation and concomitant inversion at nitrogen and rotation around the C—N bond However this process does not affect the dissymmetry at the tin center, as is reflected by the anisochronism of the benzylic protons In our opinion, this can only be explained by the process shown in Fig 6 which involves rapid interconversion between pentacoordinate species resulting from Sn-N bond dissociation * It is to be noted that the dissymmetry in the equatorial plane of these species must be similar to that of the (2-$Me_2NCHZC_6H_4$)-$RSnX_2$ species (VI—IX) discussed above

Experimental

All reactions were carried out under dry oxygen-free nitrogen Solvents were carefully purified and distilled before use under nitrogen 2-[(Dimethylamino)-methyl]phenylcopper and [1-(*S*)-(dimethylamino)ethyl]phenylcopper were prepared by published methods [4,5]

^1H NMR spectra were recorded using Varian Associates HA 100 and T 60 spectrometers and a Bruker WH 90 NMR spectrometer

Elemental analyses were carried out in the Analytical Department of the TNO institute

{2-[(Dimethylamino)methyl]phenyl}methyltin dichloride (VI)

A solution of the copper compound (IV, 1 mmol) in 20 ml of benzene was added during 15 min to a solution of 1 mmol of $MeSnCl_3$ in 20 ml of benzene, yielding a colorless solution and a white precipitate The mixture was stirred for an additional 30 min and then filtered (quantitative amount of CuCl) The solution was evaporated at reduced pressure and the resulting white solid was washed twice with two 15-ml portions of pentane and then dried under vacuum (96% yield) ^1H NMR spectroscopy indicated this compound to be pure VI. The compound was recrystallized from hot toluene Found C, 35 5, H, 4.4, Cl, 20 9, N, 4.1, Sn, 34 9. $C_{10}H_{15}Cl_2NSn$ calcd.. C, 35 45, H, 4 46, Cl, 20 93, N, 4 13, Sn, 35.03%. M p 128—130°C Mol wt (osmometry in benzene)· found (calcd.), 341 (339)

{2-(Dimethylamino)methyl]phenyl}methyltin dibromide (VII)

This compound was prepared according to the same procedure as the corresponding dichloro compound, starting from 1 mmol of the organocopper compound IV and 1 mmol of $MeSnBr_3$ (yield 98%). Found. C, 28.3, H, 3.5, Br, 37 2, N, 3 2, Sn, 27.4. $C_{10}H_{15}Br_2NSn$ calcd. C, 28 08, H, 3 53, Br, 37 36, N, 3 27; Sn, 27 75% M p 122—126°C Mol wt (osmometry in benzene) found (calcd.), 437 (427).

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* The CH_2 protons in both the coordinated and the free CH_2NMe_2 groups are diastereotopic and appear in the spectra of X as an averaged AB pattern cf ref 3

{2-(Dimethylamino)methyl]phenyl}phenyltin dichloride (VIII)

This compound was prepared (in 98% yield) in a similar fashion starting from 1 mmol of the copper compound IV and 1 mmol of $PhSnCl_3$ Found C 44.4, H, 4.3, N, 3 7, Cl, 18 3, Sn, 29 2. $C_{15}H_{17}Cl_2NSn$ calc C, 44.94, H, 4 27, N, 3 49, Cl, 17.69, Sn, 29 61% M p 145—147°C Mol wt (osmometry in benzene) found (calcd), 407 (401)

{2-[1-(S)-(Dimethylamino)ethyl]phenyl}methyltin dibromide (IX)

IX was prepared (in 95% yield) according to the procedure given for VI, starting from 1 mmol of (S)-Ar_4Cu_4 (V) and 1 mmol of methyltin tribromide Found. C, 30 1, H, 4.0, Br, 35 9, N, 3 3, Sn, 27 1. $C_{11}H_{17}Br_2NSn$ calcd C, 29 91, H, 3 88; Br, 36 18; N, 3 17, Sn, 26 87% M p 102—105°C Mol wt (osmometry in benzene). found (calcd), 450 (442)

Bis{2-[(dimethylamino)methyl]phenyl}tin dibromide (X)

A solution of the copper compound (IV, 2 mmol) in benzene (20 ml) was added during 15 min to a solution of $SnBr_4$ (1 mmol) in benzene (20 ml) yielding a white precipitate and a colourless solution The precipitate was filtered off washed with benzene (15 ml) and extracted with two 15-ml portions of chloroform. The combined chloroform solutions were concentrated and the resulting white solid was washed with 15 ml of pentane (twice) and dried under vacuum (yield 85%). Found: C, 39.4; H, 4 5; Br, 29 0; N, 5 1, Sn, 21 3 $C_{18}H_{24}Br_2NSn$ calcd : C, 39 53; H, 4.42; Br, 29 22; N, 5 12, Sn, 21 70% M.p 245—248°C Mol wt. (ebulliometry in chloroform): found (calcd.), 538 (547)

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